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Quantum Monte Carlo methods have proved remarkably successful in providing accurate predictions of energies and structures for molecular systems. These methods are 'exact' for systems of a few electrons and highly accurate for systems of as many as a thousand electrons. The scaling of computation effort with molecular size is highly favorable relative to that of other methods. The most commonly used quantum Monte Carlo methods – diffusion and Green's function – are introduced in these notes.

1 Introduction

For systems containing a few electrons – such as the molecular ion H_3^+, the dimer He-He, the trimer He_3, the pair He-H, and the molecule H_2 – a quantum Monte Carlo method provides absolute accuracies of better than 0.01 kcal/mole without systematic error. When an 'exact' potential energy surface for the reaction H + H_2 → H_2 + H is needed a quantum Monte Carlo method is the choice ... providing 60,000 points on the surface with accuracies in the range of 0.01 to 0.10 kcal/mole[1].

For systems containing hundreds of electrons – such as the electron gas, metallic lithium, clusters of carbon atoms, crystals of N_2, large molecules Si_mH_n, and solid silicon – quantum Monte Carlo methods provide the most accurate solutions available. When the stable, lowest-energy structure of C_{20} is desired a quantum Monte Carlo method gives the most reliable result.

Of course, quantum Monte Carlo methods are not so easily packaged as many other methods and they have far fewer practitioners. The program QMagiC is not as user-friendly as Gaussian98. But, there are many problems that demand solutions of very high accuracy – if only to provide benchmarks for calibrating other methods – and these are problems which demand QMC methods. The scaling of QMC methods with the number of electrons is generally favorable compared to that of other methods (see Table 1), and the scaling of QMC methods with increasing accuracy is especially favorable at high accuracies compared to that of other methods.

In these notes we describe the several quantum Monte Carlo methods and discuss their characteristics, their advantages and disadvantages. We present a representative sampling of results of QMC calculations to illustrate the range of systems which have been treated successfully. Our object is to provide an introduction together with an overview of the field.

We call attention to several prior reviews in the QMC area which give different insights and additional details. These include one book[3] of general coverage, review articles of a general nature[4–11], a review of 'exact' methods[12], a discussion of fixed-node calculations[13], and a review of applications to solids[14].

Theoretical Method	Computational Dependence on Number of Electrons	Maximum Feasible Molecular Size (atoms)
FCI	$N!$	2
CCSD(T)	N^7	$8-12$
CCSD	N^6	$10-15$
MP2	N^5	$35-50$
HF	$N^{3.5}-N^4$	$50-200$
KS-DFT	$N^{3.5}-N^4$	$50-200$
FNQMC	N^3	$50-200$

Table 1. Scaling of computation requirements with number of electrons. Based in part on a table by Head-Gordon[2].

2 History and Overview

Among the various ways in which Monte Carlo methods can be utilized in solving the Schrödinger equation there are four methods commonly termed 'quantum Monte Carlo' methods (QMC). These are the variational quantum Monte Carlo method (VQMC), the diffusion quantum Monte Carlo method (DQMC), the Green's function quantum Monte Carlo method (GFQMC), and the path integral quantum Monte Carlo method (PIQMC). These methods are by their nature strongly related and each has its own peculiar advantages and disadvantages relative to the others.

The variational method VQMC is the same as the conventional analytic variational method except that the required integrals are evaluated using special Monte Carlo methods. It has its roots in a numerical method reported by Frost[15] in 1942. In Frost's own words: "A method of approximation to the Schrödinger equation has been developed in which variation functions are used but no integrations are involved. The procedure involves evaluation of the energy for a set of representative points in configuration space. The parameters in the variation function are then chosen by applying the condition that the mean square deviation of the energy from the average should be a minimum." As a part of this calculation Frost estimated the expectation value of the energy $\langle E \rangle$ from the local energies $E_{loc} = H\Psi_0/\Psi_0$ for a trial wavefunction Ψ_0 using ${\Psi_0}^2$ as a weighting factor according to

$$\langle E \rangle = \frac{\int \Psi_0^2 \frac{H\Psi_0}{\Psi_0} d\tau}{\int \Psi_0^2 d\tau} \cong \frac{\sum \Psi_0^2 \frac{H\Psi_0}{\Psi_0}}{\sum \Psi_0^2} \quad , \tag{1}$$

where the summations are for points in the configuration space of the electrons, chosen in a manner "to be determined through experience". Frost was successful in investigating preliminary applications to a few simple molecules.

The Monte Carlo aspect of choosing points was introduced by Conroy[16] in 1964. Conroy proposed picking points at random in the configuration space of the electrons with probabilities proportional to ${\Psi_0}^2$ and equal weights. Conroy noted "If ... the density function [is] ${\Psi_0}^2$, ... then clearly optimum Monte Carlo sampling has the density of random points proportional to the density of electrons in the actual molecule." The procedure leads to a good approximation of the ratio of the integrals in Eq. (1) for a large number of points

and to the exact value in the limit of a large number of points. Conroy was able to obtain some excellent values for the energies of $H_2{}^+$, H^-, HeH^{++}, He, H_2, and Li. His calculation for Li was the first application of VQMC to a fermion system with nodes.

Conroy's VQMC calculations were followed very soon by those of McMillan[17] for liquid helium using the Metropolis algorithm to sample the configuration space for points with probabilities proportional to ${\Psi_0}^2$. Only very recently has a much more efficient method for choosing points - anticipated to some extent by Conroy - been devised[18].

The DQMC method is based on the similarity of the Schrödinger equation and the diffusion equation. It has its roots in the Monte Carlo simulation of neutron diffusion and capture by Fermi and others at Los Alamos in the 1940's. Metropolis and Ulam[19] first outlined the method in 1947: "... as suggested by Fermi, the time-independent Schrödinger equation

$$-\frac{1}{2}\nabla^2\Psi(x,y,z) = E\Psi(x,y,z) - V\Psi(x,y,z) \tag{2}$$

could be studied as follows. Re-introduce time by considering

$$\Psi(x,y,z,t) = \Psi(x,y,z)\, e^{-Et} \quad . \tag{3}$$

and $\Psi(x,y,z,t)$ will obey the equation

$$\frac{\partial\Psi(x,y,z,t)}{\partial t} = \frac{1}{2}\nabla^2\Psi(x,y,z,t) - V\Psi(x,y,z,t) \quad . \tag{4}$$

This last equation can be interpreted however as describing the behavior of a system of particles each of which performs a random walk, i.e., diffuses isotropically and at the same time is subject to multiplication, which is determined by the value of the point function V. If the solution of the latter equation corresponds to a spatial mode multiplying exponentially in time, the examination of the spatial part will give the desired $\Psi(x,y,z)$ – corresponding to the lowest 'eigenvalue' E." The first applications of DQMC to electronic systems were reported by Anderson[20] in 1975 and were followed by a large number of additional developments, along with applications to a wide variety of chemical problems.

The GFQMC method was proposed by Kalos[21] as an alternative to the DQMC method. As Kalos noted, "It seemed more natural and promising to look for an integral equation formulation of the Schrödinger equation and attempt its solution by Monte Carlo methods." The first applications of GFQMC were in determining the binding energies of three- and four-body nuclei[21]. For problems having appropriate boundary conditions and potential energy functions the GFQMC method is preferred, but it is not well suited for most electronic systems. However, it provides the basis for 'exact' (i.e., without systematic error) solutions for systems of a few electrons.

The PIQMC method is the result of coupling of Feynmann's path integral formulation of quantum mechanics[22] with Monte Carlo sampling techniques to produce a method for finite-temperature quantum systems. In the limit of zero temperature the method is closely related to the GFQMC method. The earliest applications of PIQMC were made to lattice models, but a number of applications to continuum systems of bosons have been made, including some very successful calculations of properties of liquid helium[23]. Applications to fermion systems are more difficult, but a few studies have been carried out[24].

3 Variational Quantum Monte Carlo

In the variational quantum Monte Carlo (VQMC) method the expectation value of the energy $\langle E \rangle$ and/or another average property of a system is determined by Monte Carlo integrations. The expectation value of the energy is typically determined for a trial function Ψ_0 using Metropolis sampling[25] based on Ψ_0^2. It is given by

$$\langle E \rangle = \frac{\int \Psi_0^2 \frac{H\Psi_0}{\Psi_0} d\tau}{\int \Psi_0^2 d\tau} = \lim_{n\to\infty} \frac{\sum_{i=1}^{n} \frac{H\Psi_0}{\Psi_0}}{\sum_{i=1}^{n} 1}, \tag{5}$$

where the summations are for samples of equal weights selected with probabilities proportional to Ψ_0^2. As in analytic variational calculations the expectation value $\langle E \rangle$ is an upper limit to the true value of the energy E,

$$\langle E \rangle \geq E \ . \tag{6}$$

The term $\frac{H\Psi_0}{\Psi_0}$ is a local energy E_{loc}. In determining $\langle E \rangle$ it is not necessary to carry out analytic integrations; and, since only differentiation of the trial wavefunction is required to evaluate the local energy, the trial wavefunction may take any desired functional form. It may even include inter-electron distances r_{ij} explicitly. Thus, relatively simple trial functions may incorporate electron correlation effects rather accurately and produce expectation values of the energy well below those of the Hartree-Fock limit. Except in the limit of a large number of terms the VQMC method is not an exact method.

The Metropolis sampling procedure provides a means of sampling points in configuration space with specified probabilities, in this case, with probabilities proportional to the square of the wavefunction. Starting from an arbitrary initial point, one chooses a new point at a fixed distance (or from a distribution of fixed distances) in a random direction. One then calculates the ratio of weights new-to-old, $\Psi_0^2(new)/\Psi_0^2(old)$, and accepts the move to the new point with the probability given by the ratio. If the ratio is greater than unity the move is accepted. If the move is not accepted the old point is treated as a new point. The result of a large number of iterations is a guided random walk which samples points in configuration space with frequencies proportional to Ψ_0^2. The reader might wish to consider a two-point system of a and b with weights W_a and W_b for which a near-equilibrium distribution is obtained in sampling with just a few steps.

The step sizes for a typical Metropolis walk are usually chosen to give an acceptance ratio of about one-half in order maximize the rate of 'diffusion' and improve the sampling speed. Serial correlation of points is usually high. In many-dimensional (or many-electron) systems the steps may be taken one dimension (or one electron) at a time or all at once. The optimum step sizes and/or combinations of steps depend strongly on the nature of the system treated.

The Metropolis procedure can be made more efficient by using a bias of each step in the direction of higher weight as indicated by the derivative of the weight at the old point. In the limit of small steps this leads to the Fokker-Planck equation, which is applicable to diffusion with drift and is directly related to the 'importance sampling' in diffusion quantum Monte Carlo discussed below. For many systems this type of sampling is more efficient than Metropolis sampling, but care must be taken to eliminate the time-step error[26] associated with simulation of the Fokker-Planck equation. The procedure is somewhat more

complicated, offers a greater opportunity for error, and is used less often than Metropolis sampling.

Another alternative, likely to be more efficient than Metropolis sampling, is the use of probability density functions[27]. These relatively simple functions which mimic the density of the more complex function Ψ_0^2 can be sampled directly without a Metropolis walk and the associated serial correlation. Sample points of unit weight are obtained with probabilities proportional to the probability density P and their weights are multiplied by the factor Ψ_0^2/P to give overall Ψ_0^2 weighting. The expectation value of the energy $\langle E \rangle$ is then given by

$$\langle E \rangle = \frac{\int \Psi_0^2 \frac{H\Psi_0}{\Psi_0} d\tau}{\int \Psi_0^2 d\tau} = \lim_{n\to\infty} \frac{\sum_{i=1}^{n} (\Psi_0^2/P) \frac{H\Psi_0}{\Psi_0}}{\sum_{i=1}^{n} (\Psi_0^2/P) 1} \ , \tag{7}$$

where the summations are for samples of equal weights selected with probabilities proportional to P.

4 Diffusion Quantum Monte Carlo

The diffusion quantum Monte Carlo method (DQMC) approaches the solution of the Schrödinger equation in a way completely different from that of variational methods. The basic ideas were given above in the succinct description quoted from the original paper by Metropolis and Ulam[19]. Here we give a more complete description.

The DQMC method is basically a simple game of chance involving the random walks of particles through space and their occasional multiplication or disappearance. It may be viewed as based on the similarity between the Schrödinger equation and the diffusion equation (i.e., Fick's second law of diffusion) and the use of the random walk process to simulate the diffusion process. Following the early discussions in the 1940's by Metropolis and Ulam[19] and by King[28] a number of related techniques were proposed and discussed in succeeding years, but it was not until fast computers became available that applications to multicenter chemical systems became practical[20].

The equation to be solved is the time-independent Schrödinger equation, $H\Psi = E\Psi$, or

$$-\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 \Psi(\vec{X}) + V(\vec{X})\Psi(\vec{X}) = E\Psi(\vec{X}) \ , \tag{8}$$

where the summation is over the electrons or other particles i having masses m_i and the nomenclature is standard. Since we are concerned with the time-independent Schrödinger equation the wavefunction may be treated as a real number rather than a complex number. For simplicity we consider the equation for a single particle of mass m, rearranged to become

$$\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{X}) - V(\vec{X})\Psi(\vec{X}) = -E\Psi(\vec{X}) \ . \tag{9}$$

The equation has as solutions the wavefunctions $\Psi_0(\vec{X})$, $\Psi_1(\vec{X})$, ... which exist only for specific energies E_0, E_1, ...

The wavefunction may be treated as a function of an additional variable τ defined according to

$$\Psi(\vec{X},\tau) = \Psi(\vec{X})e^{-E\tau} \ . \tag{10}$$

The function then behaves according to

$$\frac{\partial\Psi(\vec{X},\tau)}{\partial\tau} = -E\Psi(\vec{X},\tau) \tag{11}$$

and we have

$$\frac{\partial\Psi}{\partial\tau} = \frac{\hbar^2}{2m}\nabla^2\Psi - V\Psi \ . \tag{12}$$

The function $\Psi(\vec{X},\tau)$ in Eq. (11) may be considered general, but at large values of τ its solution is given by the $\Psi(\vec{X},\tau)$ of Eq. (10) corresponding to the lowest-energy or ground-state wavefunction for the system. Since higher-energy states decay faster according to Eq. (10) an arbitrary initial function consisting of a sum of terms containing the wavefunctions for the ground-state and any or all the higher states decays to the ground-state wavefunction. The arbitrary initial function evolves to the ground-state solution of the time-independent Schrödinger equation.

Because of its similarity to the time-dependent Schrödinger equation, Eq. (12) is often referred to as the Schrödinger equation in imaginary time. The analogy is formally correct since solutions of the time-dependent Schrödinger equation have equivalent real and imaginary parts under steady-state conditions.

The Schrödinger equation in imaginary time τ has the same form as the diffusion equation with an added first-order reaction term,

$$\frac{\partial C(\vec{X},t)}{\partial t} = D\nabla^2 C(\vec{X},t) - kC(\vec{X},t) \ . \tag{13}$$

The concentration C corresponds to the wavefunction Ψ, the diffusion coefficient D corresponds to the group $\frac{\hbar^2}{2m}$, and the rate constant k corresponds to the potential energy V.

Differential equations are normally used to model the behavior of physical systems and the diffusion equation above is normally used to model the behavior of a system in which particles undergo diffusion by a random walk process. In quantum Monte Carlo calculations the random walk process is used to simulate the differential equation. Of course, the connection between the random walk process and quantum mechanics may be considered to be direct. In the absence of the Schrödinger equation one might still use the Monte Carlo method to obtain solutions to quantum mechanical problems, but the connection between random walks and quantum mechanics is most easily made with the aid of the Schrödinger equation as above.

The random walk process and the diffusion equation are related through the diffusion coefficient by the Einstein equation[29],

$$D = \frac{\overline{(\Delta x)^2}}{2\Delta\tau} \ , \tag{14}$$

which gives the diffusion coefficient for particles moving a distance Δx at random positive or negative at intervals of time $\Delta\tau$. In the simulation of the Schrödinger equation in imaginary time the time and distance steps are chosen to produce the appropriate value of D (or $\frac{\hbar^2}{2m}$) given by Eq. (13).

The standard quantum mechanical problem of the harmonic oscillator may be used to illustrate the diffusion quantum Monte Carlo method. The potential energy is given by the function $V = \frac{1}{2}kx^2$. The potential energy may be shifted by an arbitrary constant energy to make V negative in the central region near $x = 0$ and positive away from the center.

An initial collection of particles, typically termed 'walkers' but occasionally termed 'psips' and perhaps a dozen other names, is distributed in the region about $x = 0$. Time is advanced one step $\Delta\tau$. To simulate the diffusion term of Eq. (13) each walker is moved right or left at random a distance Δx. To simulate the multiplication term of Eq. (13) each walker then gives birth to a new walker with a probability $P_b = -V\Delta\tau$ if V is negative or disappears with a probability $P_d = V\Delta\tau$ if V is positive. Time is advanced another step and the process is repeated. If the number of walkers falls below an acceptable lower limit or increases beyond an acceptable upper limit, their number may be adjusted by the random multiplication or removal of walkers present. (See comment below on avoiding bias with such adjustments.) For the harmonic oscillator as indicated the walkers diffuse away from the center and disappear at the sides in the regions of high potential energy, but they are replaced by walkers multiplying near the center at negative potential energies. After a large number of iterations the distribution of walkers approaches a fluctuating 'steady-state' distribution – the function $\exp(-ax^2)$ with $a = \frac{1}{2}\sqrt{k}$ – which corresponds to the wavefunction for the ground state of the harmonic oscillator.

The procedure is readily extended to problems having a higher number of dimensions and is clearly most useful for problems in which the number of dimensions is large. A system of n electrons free to move in three dimensions each can be simulated by a collection of walkers moving in $3n$ dimensions each.

For a molecule the procedure in similar. For the case of H_2 the Schrödinger equation in imaginary time for the two-electron system with both nuclei fixed is given, in atomic units, by

$$\frac{\partial\Psi}{\partial\tau} = \frac{1}{2}\nabla_1^2\Psi + \frac{1}{2}\nabla_2^2\Psi - V\Psi \ . \tag{15}$$

With the electrons labeled 1 and 2 and the two protons labeled A and B the potential energy V, exclusive of the internuclear term, is

$$V = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} \ , \tag{16}$$

in which r_{1A} is the distance between electron 1 and proton A and so forth. It is convenient to introduce a reference potential V_{ref} so that the operating equation becomes

$$\frac{\partial\Psi}{\partial\tau} = \frac{1}{2}\nabla_1^2\Psi + \frac{1}{2}\nabla_2^2\Psi - (V - V_{ref})\Psi \ . \tag{17}$$

In terms of the diffusion equation we then have D = 1/2 and $k = (V - V_{ref})$.

The random walk in six dimensions is usually executed with non-uniform step sizes in each dimension selected from a Gaussian distribution with probabilities P of step sizes

Δx given by

$$P(\Delta x) = \frac{1}{\sqrt{2\pi}\sigma} exp(-\frac{(\Delta x^2)}{2\sigma^2}) \ . \tag{18}$$

The probability of birth is given by $P_b = -(V - V_{ref})\Delta\tau$ for $(V - V_{ref})$ less than zero and the probability of disappearance is given by $P_d = (V - V_{ref})\Delta\tau$ for $(V - V_{ref})$ greater than zero. After each move a random number in the interval (0,1) for each walker is compared with P_b (or P_d) and if smaller than P_b (or P_d) then a birth (or death) is completed.

A calculation is begun with a collection of 1000 or more walkers in positions corresponding to electron configurations in the region of the nuclei and allowed to approach the steady-state distribution. The step size is then fixed at a small value to improve the accuracy of the results in the accumulation of data after steady-state is reached.

In order to maintain the number of walkers approximately constant the arbitrary reference potential V_{ref} may be adjusted occasionally, but to avoid bias a large delay prior to adjustment is advised. At steady-state the energy E corresponding to a wavefunction Ψ may be evaluated using Eq. (11) rearranged as

$$E = -\frac{1}{\Psi}\frac{\partial\Psi}{\partial\tau} \ . \tag{19}$$

For a given distribution the wavefunction is proportional to the total number of walkers N and one has

$$E = -\frac{1}{N}\frac{\partial N}{\partial\tau} \ . \tag{20}$$

In the case of the ground state of H_3^+ , which has no boundaries serving as sinks or sources for walkers, the total number of walkers is not directly affected by the diffusion terms of Eq. (17) but changes according to

$$\frac{\partial N}{\partial\tau} = -\sum_N (V - V_{ref}) \ . \tag{21}$$

The energy is thus given by the average potential energy $\overline{V}$ according to

$$E = \overline{V} \ . \tag{22}$$

After steady-state is reached the energies at each time step are retained for a subsequent determination of the overall average for a large number of samples.

There are five important sources of error in these first diffusion Monte Carlo calculations: (a) Statistical or sampling error associated with the limited number of independent sample energies used in determining the energy from an average of variable potential energies, (b) the use of a finite time-step $\Delta\tau$ rather than an infinitesimal time-step as required for the exact simulation of a differential equation, (c) numerical error associated with truncation and/or round-off in computing, (d) imperfect random number quality, (e) failure of the distributions to reach the steady-state or equilibrium distributions in a finite number of steps. Sources (c), (d), and (e) are common problems in computing. They can be detected relatively easily and eliminated, and they are not found to limit the calculations in any significant way. Sources (a) and (b) seriously limit the accuracy of most DQMC calculations, but twenty years of refinement of methods to reduce time-step error as well as the higher speeds of computers have reduced greatly the magnitude of these errors and uncertainties.

For systems containing two or more electrons of the same spin or other indistinguishable particles, an additional problem appears: the node problem. For these systems it is necessary to restrict the form of the total wavefunction (space and spin parts) such that it is antisymmetric to the exchange of electrons. For any electronic state other than the ground state it is necessary to restrict further the properties of the wavefunction. The effect of these restrictions is the imposition of nodal surfaces, on which $\Psi(\vec{X}) = 0$, in the space part of the wavefunction. For systems of a few electrons the node problem can be overcome by exact cancellation methods (described below) and solutions free of systematic error can be obtained. For systems of more than a few electrons the fixed-node method, which in not an exact method, is usually required.

5 Green's Function Quantum Monte Carlo

For certain boundary conditions the diffusion equation may be solved with the use of standard Green's function methods, and the diffusion equation with an added first-order reaction term may be treated by these methods. The Green's function quantum Monte Carlo method is similar to the DQMC method but takes advantage of the properties of Green's functions in eliminating time-step entirely in treating the steady-state equation. The GFQMC method makes possible very large step sizes, but some of the advantages of large steps are lost for fixed-node calculations. The Green's function quantum Monte Carlo method was proposed by Kalos[21] for nodeless systems. Procedures for introducing fixed nodes were developed later.

The time-independent Schrödinger equation, Eq. (9), may be written in the form

$$-\nabla^2\Psi(\vec{X}) + k^2\Psi(\vec{X}) = k^2\frac{V(\vec{X})}{E}\Psi(\vec{X}) \ , \tag{23}$$

where

$$k^2 = -\frac{2mE}{\hbar^2} \ . \tag{24}$$

To keep k^2 positive the energy must be made negative. This can be done by adjusting the reference or zero of the potential energy by an appropriate offset of energy.

The Green's function for Eq. (9) which satisfies the boundary conditions for a problem in electronic structure (i.e., $\Psi \rightarrow 0$ as $X \rightarrow \infty$) is known and is given by

$$G(\vec{X},\vec{X}') = \frac{1}{(2\pi)^{\frac{3N}{2}}}K_{\frac{3N}{2}-1}(k|\vec{X}-\vec{X}'|)/(k|\vec{X}-\vec{X}'|)^{\frac{3N}{2}-1}, \tag{25}$$

where K_ν is the modified Bessel function of the second kind.

The Green's function method is carried out iteratively with steps analogous to time steps. Repetitive sampling is based on the property of the Green's function which reproduces the wavefunction from itself,

$$\Psi(\vec{X}) = \int G_o(\vec{X},\vec{X}')\frac{V(\vec{X}')}{E}\Psi(\vec{X}')d\vec{X}' \ . \tag{26}$$

The repeated application of Eq. (26) to an initially arbitrary wavefunction $\Psi(\vec{X}')$ produces a wavefunction $\Psi(\vec{X})$ which is the lowest-energy solution to the Schrödinger equation for

the boundary conditions specified. A walker in the distribution $\Psi(\vec{X}')$ may be transferred to the distribution $\Psi(\vec{X})$ by multiplying its weight by $\frac{V(\vec{X}')}{E}$, sampling the Green's function distribution $G_o(\vec{X}, \vec{X}')$, and moving the walker to its new position $\vec{X}$. Repetition for an initially arbitrary collection of walkers leads to a set of walkers which is a sample of points from the lowest-energy wavefunction for the boundary conditions and any other constraints imposed. As in DQMC the calculations must be carried out until a 'steady-state' distribution is obtained and sampling is carried out by continuing the calculations.

The imposition of additional boundaries corresponding to nodes for fixed-node calculations has been described by Ceperley[30], by Skinner et al.[31], and by Moskowitz and Schmidt[32]. The procedures involve conditional sampling together with smaller steps for walkers in the vicinity of the nodes.

6 Node Structure

The structure and properties of the nodal hypersurfaces of the wavefunctions for atomic and molecular systems have received very little attention. In analytic variational calculations the wavefunctions obtained are seldom examined and although electron densities are often examined, these reveal little or nothing about the node structure. Examination of the basis set of a determinantal wavefunction also reveals little or nothing because the many operations of the determinant scramble the properties of the basis functions. Only recently, with a knowledge of node structure required for developing Monte Carlo methods, have the structure and properties of nodal hypersurfaces been examined in detail.

For a system of either bosons or fermions the wavefunction must have the correct properties of symmetry and antisymmetry. Except in the simplest cases the wavefunction for a system of n fermions is positive and negative in different regions of the $3n$-dimensional space of the fermions. The regions are separated by one or more $(3n-1)$-dimensional hypersurfaces which cannot be specified except by solution of the Schrödinger equation.

The procedures described above for DQMC and GFQMC lead to the lowest-energy solutions for boson systems which are nodeless ground-state wavefunctions. They also lead to the ground-state in the case of two electrons (fermions) of opposite spin for which the wavefunction is symmetric to the exchange of the two electrons. For a system of two or more electrons of the same spin the wavefunction must be antisymmetric to the exchange of electrons of the same spin and must contain one or nodal hypersurfaces. The treatment of systems with nodes requires that the solutions be constrained to the appropriate antisymmetry.

Several properties should be noted for a system of two electrons of the same spin. The configuration space of the electrons is divided in half by the nodal surface. The two halves are similar in shape and are nested together face-to-face. The positions of the two electrons are represented by a single point in configuration space and interchange of the two electrons moves the point across the nodal surface to a similar position in the other half of configuration space.

One of the simplest cases is that of the 1s2s ^{3}S helium atom for which the wavefunction may be regarded as a function of the electron-nucleus radii r_1, r_2 and the angle θ between them. The nodal surface is the 5-dimensional hypersurface on which the electron-nucleus distances r_1 and r_2 are equal to each other. It is completely specified by the symmetry

of the function. In this case the (r_1, r_2, θ) configuration space is divided by the nodal surface into two equivalent sections, one with the wavefunction positive and one with the wavefunction negative. This is the nodal structure given by the simplest single-determinant wavefunction Ψ = 1s(1)2s(2) − 1s(2)2s(1). For $r_1 = r_2$ the wavefunction is zero and the nodal surface occurs for $r_1 = r_2$ regardless of the functions 1s and 2s provided they are functions of r_1 only and r_2 only.

In the case of 1s2p ^{3}P helium the situation is not so simple. For 1s2p ^{3}P He the symmetry properties alone are insufficient to specify the node structure. The node structure is not determined by geometric symmetry alone because there are many possible wavefunctions which have the required anti-symmetry on reflection in the $z = 0$ plane and on exchange of electrons. The simplest is given by Ψ = 1s(1)2p(2) − 1s(2)2p(1). But, there is an infinite number of different 1s and 2p functions which may be used and the node structures of the resulting wavefunctions are different. Thus, the symmetry properties alone are insufficient to specify the node structure for this case.

A detailed examination[33] has been made of the node structure of 1s2p ^{3}P helium for very accurate wavefunctions. It should be noted that the nodal surface is not a simple plane passing through the origin in the three-dimensional space of one or the other of the electrons. The wavefunction is not the product function Ψ = 2s(1)2p(2) and its node structure is not that of the product function. The node structure is similar to that of the determinantal function and very much different from that of the product function.

DQMC calculations for atoms and molecules such as H_2, H_4, Be, H_2O, and HF using fixed-node structures obtained from optimized single-determinant SCF calculations typically recover more than 90 percent of the correlation energies of these species and yield total electronic energies lower than the lowest-energy analytic variational calculations. These results suggest that optimized single-determinant wavefunctions have node structures which are reasonably correct.

An investigation of the node structure of the wavefunction in the 30-dimensional configuration space of a 10-electron molecule is not an easy task, but it has been carried out for the water molecule. The node structure for the ground state is that suggested by earlier investigations for smaller systems. For a molecule with *m* spin-up electrons and *n* spin-down electrons the node structure is approximately that of the product of two functions, one for spin-up and the other for spin-down electrons. The $3m$-dimensional configuration space of spin-up electrons is divided by a $(3m - 1)$-dimensional nodal hypersurface into two geometrically similar regions nested together face-to-face. The $(3n - 1)$-dimensional nodal hypersurface for the spin-down electrons has equivalent characteristics.

7 Importance Sampling

One very important means of improving the accuracies is the technique called "importance sampling" which was introduced by Grimm and Storer[34] in 1971. As is clear from their work, one should be able to take advantage of prior knowledge of the properties of wavefunctions to make quantum calculations of many types more efficient. Such prior knowledge is available in the form of wavefunctions from analytic variational calculations at several levels of approximation. It is possible to obtain very high accuracies by extending diffusion quantum Monte Carlo calculations to calculate corrections to trial wavefunctions rather than the complete wavefunction. We discuss those correction methods in a separate

section.

To obtain the importance-sampling version of diffusion quantum Monte Carlo, we first multiply the basic equation, Eq. (4) by a trial wavefunction Ψ_t and define a new term $f = \Psi\Psi_t$ which is the product of the true wavefunction and the trial wavefunction. After several pages of rearrangement we obtain the basic equation for DQMC with importance sampling,

$$\frac{\partial f}{\partial \tau} = \frac{\hbar^2}{2m}\nabla^2 f - \nabla \cdot (f \nabla \ln \Psi_t) - E_{loc} f \ . \tag{27}$$

The equation has terms on the right side corresponding to diffusion of walkers with a diffusion coefficient of $\frac{\hbar^2}{2m}$, a drift term with a velocity given by $\nabla \ln \Psi_t$, and a first-order rate term for the disappearance of walkers with a rate constant given by the local energy $E_{loc} = \frac{H\Psi_t}{\Psi_t}$ for the trial wavefunction.

In DQMC the simulation of Eq. (27) is carried out in the same way as the simulation of Eq. (9) except that additional walker movement is required by the drift term and walker multiplication depends on the local energy rather than the potential energy. The diffusion and drift terms can be separately simulated. If the trial function is simply a constant the drift term is zero, the local energy is equal to the local potential energy, and the expression reduces to that for diffusion without importance sampling.

The drift term acts to produce a drift of walkers in the direction of higher Ψ_t. The walkers are thus concentrated in the more important regions and their distribution, if Ψ_t is accurate, approximates that of Ψ^2, the square of the true wavefunction. In the vicinity of a nodal surface the velocity, which may be written as $\frac{\nabla\Psi_t}{\Psi_t}$, is increased and as Ψ_t approaches zero at the nodal surface, the drift velocity approaches infinity in a direction away from the surface. Walkers are thus prevented from crossing the nodes of the trial function.

The computation procedure for diffusion with drift is similar to that of the basic random walk procedure described above. At each time step the values of $E_{loc} = \frac{H\Psi_t}{\Psi_t}$ and the drift velocity $\nabla \ln \Psi_t$ must be determined from the potential energy and from the first and second derivatives of the trial wavefunction. The drift distance is given by the product of the vector drift velocity and the time step. Multiplication is based on the local energy.

A calculation generates a distribution of walkers with a concentration corresponding to the value of the function $f = \Psi\Psi_t$. For the determination of energies an average of local energies is used. Following Grimm and Storer[34] one can obtain the expression giving the energy as the average of local energies for the f-particles or walkers. Multiplying the time-independent Schrödinger equation by the trial function we obtain at any point

$$\Psi_t H \Psi = \Psi_t E \Psi \ . \tag{28}$$

Integrating over all space yields

$$\int \Psi_t H \Psi dX = \int \Psi E \Psi_t dX \ . \tag{29}$$

The Hermitian properties of wavefunctions, for identical boundary conditions and symmetries, allow a permutation to yield

$$\int \Psi H \Psi_t dX = \int \Psi E \Psi_t dX \ , \tag{30}$$

which may be rewritten as

$$\int \Psi\Psi_t \frac{H\Psi_t}{\Psi_t} dX = E \int \Psi\Psi_t dX \quad . \tag{31}$$

This may be rearranged to give the energy as

$$E = \frac{\int \Psi H \Psi_t dX}{\int \Psi\Psi_t dX} \tag{32}$$

or

$$E = \frac{\int f E_{loc} dX}{\int f dX} \quad . \tag{33}$$

The equivalent Monte Carlo expression, for equally weighted samples based on f, gives the energy as the average of local energies,

$$E = \frac{\sum \frac{H\Psi_T}{\Psi_T}}{\sum 1} = \frac{\sum E_{loc}}{\sum 1} \quad . \tag{34}$$

The first applications in diffusion Monte Carlo were made for the nodeless ground state of the molecular ion H_3^+[35]. The effect was a subtantial improvement in accuracy from an energy of -1.3414 ± 0.0043 hartrees in an earlier calculation to -1.3439 ± 0.0002 hartrees in a similar calculation using importance sampling. The statistical error is reduced by a factor of about 20 and any systematic error is presumed to be similarly reduced.

The nodes of the trial function become the fixed nodes of the wavefunction Ψ which is the exact solution for the Schrödinger equation for boundary conditions corresponding to the fixed nodes. As for simple diffusion with fixed nodes the energy determined is an upper bound to the true energy.

Importance sampling may also be incorporarted into GFQMC calculations. Although GFQMC calculations must treat walkers corresponding to the wavefunction Ψ itself rather than the product $\Psi\Psi_0$, one can repeatedly 'split' and/or 'kill' the Ψ-walkers to adjust their weights to be approximately inversely proportional to the local value of Ψ_0. If this is done the individual weights in the summations of Eq. (34) may be made approximately equal and the calculations made reasonably efficient.

8 Trial Wavefunctions

In VQMC the accuracy of the trial function determines directly the accuracy in the energy obtained in a calculation. With importance sampling in either DQMC or GFQMC for systems without nodes the energy determined is, in principle, independent of the trial function, and only the uncertainty in the energy depends on the trial function. With fixed-node DQMC or GFQMC methods applied to systems with nodes the accuracy in the energy depends only on the accuracy of the node locations, and the uncertainty in the energy depends on the overall accuracy of the entire wavefunction. In any case, a more accurate trial wavefunction will improve a calculation by reducing the statistical uncertainty, by lowering the energy toward the exact value, and/or by reducing the extent of any systematic error such as time-step error.

The ideal trial wavefunction is simple and compact, has simple easily evaluated first and second derivatives, and is accurate everywhere. Since the local energy must be evaluated repeatedly the computation effort required for the derivatives makes up a large part of the overall computation effort for many systems. The typical trial wavefunctions of analytic variational calculations are not often useful, since they are severely restricted in form by the requirement that they be amenable to analytic integrations. The QMC functions are essentially unrestricted in form since no analytic integrations are required. First and second derivatives of trial wavefunctions are needed, but differentiation is in general much easier than integration and most useful trial wavefunctions have reasonably simple analytical derivatives. In most analytic variational calculations to date it has not been possible include the interelectron distances r_{ij} in the trial wavefunction and these wavefunctions are not usually "explicitly correlated", but for QMC calculations of all types "explicitly correlated" functions containing r_{ij} are the norm.

A simple wavefunction for H_2 in its ground elctronic state may be written as

$$\Psi_0 = (e^{-ar_{1A}} + e^{-ar_{1B}})(e^{-ar_{2A}} + e^{-ar_{2B}})e^{\frac{br_{12}}{1+cr_{12}}}. \tag{35}$$

In this the uncorrelated product of the two one-electron terms containing the electron-nucleus distances r_{iN} is multiplied by a Bijl or Jastrow function[36] incorporating r_{ij},

$$J = e^{\frac{br_{ij}}{1+cr_{ij}}}. \tag{36}$$

For most molecules even the simplest of trial wavefunctions is remarkably accurate. For hydrocarbons a single-determinant SCF function constructed with a minimal basis set and mildly optimized has an expectation value for the energy which corresponds to about 99 percent of the true energy. The nodes of these functions are also remarkably accurate and may be incorporated in functions giving 99.99 percent of the true energy[37]. That is not quite good enough in many cases – an error of 0.01 percent for methane corresponds to 2.5 kcal/mole – but it is a very good start.

The typical trial wavefunction for QMC calculations on molecular systems consists of the product of a Slater determinant multiplied by a second function which accounts to some extent for electron correlation with use of interelectron distances. The trial wavefunctions are most often taken from relatively simple analytic variational calculations, in most cases from calculations at the SCF level. Thus, for the 10-electron system methane[37] the trial function may be the product of the SCF function, which is a ten-by-ten determinant made up of two five-by-five determinants, and a Jastrow function for each pair of electrons,

$$\Psi_0 = \mathrm{det}^{\mathrm{up}}\mathrm{det}^{\mathrm{down}}\mathrm{exp}\left(\sum_{i<j}\frac{br_{ij}}{(1+cr_{ij})}\right). \tag{37}$$

The values of b and c may be specified as 1/2 for pairs of electrons with opposite spins and as 1/4 for pairs with identical spins. This avoids infinities in the local energy for two electrons at the same position. The Jastrow functions incorporate the main effects of electron-electron interactions and give a significant improvement over simple SCF trial functions.

More accurate, more flexible expressions are available and these have been used with

considerable success. Schmidt and Moskowitz[38] explored functions of the type

$$\Psi_0 = \det^{\rm up}\det^{\rm down}\exp\left(\sum_{i<j}\sum_k c_k(q_i^n q_j^l + q_j^n q_i^l)q_{ij}^m\right) \tag{38}$$

in which n, l, and m are integers varying with k, and $q = r/(r + 1.0)$. This particular form has been evaluated by Schmidt and Moskowitz[38] for a variety of molecular systems, and it has been used recently by Lüchow and Anderson[39] for first-row hydrides and by Alexander and Coldwell[40] for atomic systems. Modifications and extensions of the Schmidt-Moskowitz functional form have been investigated by Umrigar, Nightingale, and Runge[26] and by Alexander and Coldwell[40].

A variety of functional forms has been used for several very small systems. These include the molecules H_2, the ion H_3^+, and the dimer He-He for which Hylleraas functions, Singer polymals, and explicitly correlated Gaussian functions of very high accuracies have been used in QMC of all types.

The optimization of these functions has usually been carried out using the technique of minimizing the variance in local energies described by Conroy[16] in the 1960's. In fact, it has only rarely been done in any other way.

9 Fixed-Node Calculations

The problem of node locations – the "sign problem in quantum Monte Carlo" – remains one of the major obstacles to obtaining exact solutions for systems of more than a few electrons. In analytic variational calculations and in VQMC the locations of the nodal surfaces of a trial function may be and usually are optimized along with the rest of the wavefunction in the attempt to reach a minimum in the expectation value of the energy. In DQMC and GFQMC the node locations are not so easily varied. For systems of a few electrons – excited H_2[41], H-H-H[42,43], He-He[44,45], H-He[46] – the node problem can be overcome by exact cancellation methods[40] (described below) and 'exact' solutions (i.e., solutions free of systematic error) can be obtained. But, in general, the method of choice for systems of more than about ten electrons is the fixed-node method. Although the fixed-node method is variational in nature and does not yield exact results, it is the only choice available for quantum Monte Carlo calculations on many larger systems. The fixed-node method is remarkably accurate, and it generally yields energies well below those of the best available analytic variational calculations.

The fixed-node method was first applied in DQMC calculations for the systems H ^{2}P, H_2 $^3\Sigma_u{}^+$, H_4 $^1\Sigma_g{}^-$, and Be ^{1}S[47]. The results indicated that very good energies could be obtained with node locations of relatively poor quality. Since the nodal surfaces of ground-state systems may be expected to be located in regions of low electron density (i.e., Ψ_0^2), one might expect the calculated energies to be insensitive to small departures in node locations from those of the true wavefunctions.

The fixed-node method is easily demonstrated for the case of the first excited state of a particle in a two-dimensional rectangular box. The true wavefunction has a nodal surface which is a line dividing the region into two rectangles - one in which the wavefunction is positive and the other in which the wavefunction is negative. The wavefunction is zero at the nodal line. A DQMC calculation performed for the positive region or for the negative

region using the true node line as a boundary on which the wave function is zero will produce the true wavefunction and energy for either region. If the true wavefunction is not known in advance, then similar calculations may be made in the same way using the node line of an approximate wavefunction. The energies for the two regions must be the same and for many systems and particularly for electronic systems, this can be assured by choosing a nodal surface which divides the overall space into two regions of the same shape so that one calculation is sufficient to determine the wavefunction and energy for both. The Schrödinger equation is solved exactly within the boundaries.

Unless the assumed nodal surface is exactly correct the overall wavefunction will not be exactly correct and the energy obtained will be an upper bound to the true energy. The fixed-node method is thus variational with respect to node locations. If the nodes are wrong the calculated energy will be higher than the true energy. Approximately correct nodal surfaces are most readily available from approximately correct wavefunctions provided by analytic variational calculations.

Fixed-node calculations may be carried out using the simple diffusion quantum Monte Carlo procedure described above. The nodal surface typically divides the configuration space into identical regions such that a calculation in only one region is required. The boundary condition of $\Psi = 0$ at the nodal surface is enforced by eliminating (killing) any walker which diffuses across a node. Energies may be calculated from the growth rate as described above using Eq. (19), but Eq. (20) is not applicable since walkers may disappear at the boundaries.

The molecule H_2 in its triplet state ${}^3\Sigma_u{}^+$ was one of the first molecules to be treated using the fixed-node quantum Monte Carlo method and it serves as a simple example. It has two electrons of like spin and a single nodal surface of five dimensions in the six-dimensional configuration space of the electrons, but because of symmetries the nodal surface is easily illustrated. The early variational calculations of James, Coolidge, and Present[48] give a fairly good energy and a reasonably accurate wavefunction for an internuclear distance of 1.6 bohrs. Their calculations were made with a number of approximate wavefunctions of increasing complexity and flexibility.

Fixed-node calculations[47] for H_2 ${}^3\Sigma_u{}^+$ at an internuclear separation of 1.4 bohrs were carried out using a nodal surface given by $\Psi = 0$ for $z_1 = z_2$ as suggested by the analytical wavefunctions. The value obtained for the energy, -0.79 ± 0.01 hartrees, was in good agreement with the value of -0.7831 hartrees obtained in analytic variational calculations by Kolos and Roothaan[49] and a more accurate value -0.7842 hartrees from more recent calculations[41].

10 Exact Cancellation Method

The exact cancellation method overcomes the node problem for small systems and is thereby able to provide 'exact' solutions, i.e., solutions without systematic error and free of any physical or mathematical assumptions beyond those of the Schrödinger equation itself. The method has been applied successfully to a number of systems such as H-H-H, He-He, He-H, and He-He-He[41–46].

The method was proposed first by Arnow, Kalos, Lee, and Schmidt[50] in 1982 and was developed further with several practical improvements[41] in 1991. We describe the improved method here. In its latest form it incorporates some of the best features of fixed-

node, released-node, and other cancellation methods. It takes full advantage of the symmetric and antisymmetric properties of wavefunctions and it offers pairwise cancellations of walkers as well as self-cancellations and multiple collective cancellations.

The basic idea of cancellation is most easily illustrated with the case of the first excited state of the one-dimensional harmonic oscillator. A quantum Monte Carlo calculation for the excited state can be carried out with positive and negative walkers, initially separated left and right of center. In the absence of cancellation the two populations spread throughout the available configuration space, penetrate each other, and independently approach the symmetric distribution for the ground state. If positive and negative walkers in close proximity are occasionally allowed to cancel each other, the two populations tend to cancel each other and produce separated distributions in which the net population on the left of center is positive and that on the right of center is negative. Without any control a fluctuation in populations will eventually lead to the dominance of either positive or negative walkers and a ground-state distribution all positive or all negative. But, if the two populations are controlled to maintain equal numbers of positive and negative walkers and if cancellations are properly executed, the net distribution evolves to that of the first excited state with the node at the center.

There are several ways of cancelling positive and negative particles. Some of these are rigorously correct but not efficient and some are efficient but not rigorously correct. One might cancel positive and negative particles occupying the same position, but the probability of two walkers occupying the same position is vanishingly small. For a one-dimensional system such as the harmonic oscillator one could efficiently cancel walkers passing each other, but that opportunity is not available for systems of higher dimensionality. One might cancel walkers within an arbitrary distance of each other, but that would lead to a bias in the distributions. Fortunately, there is one way which is rigorously correct and reasonably efficient for systems of a few electrons: cancellation on the basis of the overlap of the distributions to which the walkers are moved, specifically on the basis of Green's functions in GFQMC.

The distributions of weights for two walkers with weights W_1 and W_2 and and Green's functions G_1 and G_2 overlap by an amount O_{lap} given by

$$O_{lap} = \int Min(W_1 G_1, W_2 G_2) dX, \tag{39}$$

where $Min(W_1 G_1, W_2 G_2)$ is the smaller of $W_1 G_0(X, X_1')$ and $W_2 G_0(X, X_2')$. If the distance R separating the two walkers at positions X_1' and X_2' is zero the overlap is equal to the lesser of the two weights. For large separations the overlap approaches zero.

The partial cancellation of a pair of walkers may be carried out by a Monte Carlo procedure which may be generalized to multiple collective cancellations if desired.

The move for the first walker of the pair is selected unconditionally from the distribution $G_0(X, X_1')$ and its weight at the new position X_1 becomes

$$W_1(new) = \frac{Max([s_1 W_1 G_1 - s_2 W_2 G_2], 0)}{s_1 G_1}. \tag{40}$$

The move for the second walker is treated similarly and its new weight is given by

$$W_2(new) = \frac{Max([s_2 W_2 G_2 - s_1 W_1 G_1], 0)}{s_2 G_2}. \tag{41}$$

Two walkers of the same weight and opposite sign at the same position cancel completely. In the limit of large separation the Green's function for the partner's move falls to zero and each walker keeps its original weight.

For the exact cancellation on the basis of overlapping Green's functions to be useful cancellations must occur often enough to maintain an adequate ratio of positive to negative walkers in regions where the wavefunction is positive and a similar ratio of negative to positive walkers in regions where the wavefunction is negative. Since there are multiple steady-state solutions for the ground state, fluctuations can shift the system from one solution to the other. In the case of the harmonic oscillator one solution is left-positive/right-negative and the other is left-negative/right- positive. To prevent shifts from one to the other and the resulting loss of information there must be an adequate number of walkers as well as an adequate cancellation rate. The required number of walkers and the required cancellation rate depend on the system investigated. Some systems are inherently more stable than others.

The energy for collections of positive and negative walkers may be determined with the aid of an importance sampling trial function having the same symmetry properties imposed on the collection. Equation (4) may be applied directly and, with the use of signs and weights, becomes

$$E = \frac{\sum s_i W_i \Psi_{0i} (\frac{H\Psi_0}{\Psi_0})_i}{\sum s_i W_i \Psi_{0i}} \quad , \tag{42}$$

where the summation is over all walkers.

The most efficient calculations are those for which the sum of positive products $\Psi\Psi_0$ (or $s_i W_i \Psi_{0i}$) is large compared to the sum of negative products $\Psi\Psi_0$ (or $s_i W_i \Psi_{0i}$). This gives the highest signal-to-noise ratio in computing the energy.

The obvious way of increasing walker density to produce a high signal-to-noise ratio is to increase the number of walkers up to the limit of available computer memory. Beyond that one can make full use of symmetry to concentrate walkers in a single region of configuration space. For example, a system with rotational symmetry can be rotated to place a specific electron of a walker configuration in a specific plane. This decreases the distance R between them and increases the overlap O_{lap}. Similarly, electrons of the same spin can be ordered spatially by even numbers of permutations without changing the sign of their walker.

The choice of E affects the ratio of positive to negative walkers in several ways. Since E can be adjusted by arbitrary shifts in the zero of potential energy it can be chosen to optimize the ratio. The multiplication term (V/E) can switch the sign of a walker when the V is positive and E is negative. Since E must be negative the switching of signs can be reduced by shifting the zero of potential energy to make V negative in most regions of configuration space.

With increasing numbers of electrons the cancellation rate falls rapidly and beyond about four electrons, except in special cases, exact cancellation calculations become unstable. The the 4-electron system LiH is difficult to treat, but the 8-electron He_4 system with usually well-separated atoms is well within the range of such calculations.

11 Difference Schemes

The difference δ between a true wavefunction Ψ and a trial wavefunction Ψ_0 may be determined directly in quantum Monte Carlo calculations. For an analytic trial function from any source the difference δ may be calculated and used to correct the trial function to obtain a wavefunction of higher accuracy and a more accurate eigenvalue. Successive corrections offer the possibility of unlimited accuracies. Thus far, the number of applications has been very few and the method has not been utilized in treating the problem of node locations, but difference methods offer some very interesting opportunities.

For many atomic and molecular systems approximate wavefunctions are easily obtained from SCF calculations with modest basis sets and the expectation values of the energies for these wavefunctions are typically within a few percent of the exact energies. Unfortunately, this is not good enough for most purposes. Nevertheless, such a wavefunction contains a significant amount of information and can provide a starting point for more accurate calculations.

Importance sampling, difference schemes, and their combinations all have the desirable characteristic of giving small errors for good trial wavefunctions and no errors in the limit of exact trial wavefunctions. Difference calculations have the additional desirable characteristic of correcting good trial wavefunctions to obtain better ones. Rather than calculate a complete wavefunction one may calculate the much smaller correction to a trial wavefunction. The statistical error normally associated with Monte Carlo calculations may then be limited to the correction term and thus reduced in size.

The difference method has been reported in two forms: first for simple diffusion QMC[51] and second for importance sampling diffusion QMC with drift[52]. In the case of simple diffusion one calculates the difference δ between a true wavefunction Ψ and a trial wavefunction Ψ_0 defined according to

$$\delta(X,\tau) = \Psi(X,\tau) - \Psi_0(X,\tau). \tag{43}$$

Substituting for Ψ in Eq. (4) and specifying Ψ_0 as fixed in time we obtain an equation for the change in δ with time

$$\frac{\partial \delta}{\partial \tau} = \frac{\hbar^2}{2m}\nabla^2\delta - V\delta + [\frac{\hbar^2}{2m}\nabla^2\Psi_0 - V\Psi_0]. \tag{44}$$

The equation is similar to Eq. (4). In addition to the diffusion and multiplication terms of Eq. (4) it has the term in brackets which corresponds to a distributed source fixed in time but varying with position.

As in simple diffusion QMC it is convenient to define the potential energy V of Eq. (44) with respect to a reference energy E_{ref}. With this Eq. (44) becomes

$$\frac{\partial \delta}{\partial \tau} = \frac{\hbar^2}{2m}\nabla^2\delta - (V - E_{ref})\delta + S. \tag{45}$$

The source term $S(X)$ may also be written in terms of the local energy $E_{loc} = H\Psi_0/\Psi_0$ at X for the trial wavefunction. The source term then becomes

$$S(X) = [-(E_{loc} - E_{ref})\Psi_0]. \tag{46}$$

The source term has the desirable property that as Ψ_0 approaches the true wavefunction and E_{ref} is adjusted to to equal the true energy E the term approaches zero everywhere.

The procedure for determining δ is that same as that determining Ψ directly except that additional walkers are fed to the system at each time step as required by the source term. Additional walkers are fed to the system with a probability proportional to $|S|\Delta\tau$ at each point in space. These may be positive- or negative-valued depending on the local sign of S. When the reference energy E_{ref} is adjusted to maintain a fixed net weight (normally zero) of walkers their distribution approaches that of the function δ.

The continued feed of positive and negative δ-walkers leads in time to a large number of walkers in the system and it is necessary to control their number in some way. Cancellation of of positive and negative walkers beyond a specified age – i.e., elapsed time since being fed – is perhaps the simplest means. With increasing age walkers fed at any location tend to the same distribution and they may be selected at random for cancellation. The energy E associated with a steady-state distribution may be evaluated from the reference energy E_{ref} required to maintain a fixed net weight of walkers.

The possibilities for successive corrections are apparent. The difference δ_1 determined in a calculation with an input trial wavefunction Ψ_0 may be added to Ψ_0 to obtain an improved trial wavefunction Ψ_1. This, in turn, may be used as the input for a second calculation yielding a and a second correction δ_2. The procedure may be extended to produce a series of functions $\Psi_1, \Psi_2, \Psi_3, \cdots$ of increasing accuracy.

The simple difference scheme above may be combined with the importance sampling method of Grimm and Storer[34]. A new difference function, corresponding to the difference between the products $\Psi\Psi_0$ and $\Psi_0\Psi_0$, is defined as

$$g = (\Psi - \Psi_0)\Psi_0 \ . \tag{47}$$

When Eq. (47) is introduced to Eq. (27) we obtain upon rearrangement an equation for the feed, diffusion, drift, and multiplication of g-walkers,

$$\begin{aligned}\frac{\partial g}{\partial \tau} = \frac{\hbar^2}{2m}\nabla^2 f - \nabla\cdot(f\nabla \ln \Psi_0) - (\frac{H\Psi_0}{\Psi_0} - E_{ref})\, g \\ +[-(\frac{H\Psi_0}{\Psi_0} - E_{ref}){\Psi_0}^2]\end{aligned} \tag{48}$$

When Ψ_0 approaches the true wavefunction and E_{ref} approaches E, the feed and multiplication terms both approach zero.

The last term in Eq. (48) is the source term S which may be written as

$$S(X) = [-(E_{loc} - E_{ref}){\Psi_0}^2] \tag{49}$$

or, in a more convenient form using the expectation value of energy E_{var},

$$S(X) = [-(E_{loc} - E_{var}){\Psi_0}^2] + [-(E_{var} - E_{ref}){\Psi_0}^2]. \tag{50}$$

The procedure for determining the difference term g is similar to that for determining the difference δ described above. In this case, however, the g-walkers are subject to drift as in a conventional importance sampling calculation to determine f. As in calculating δ it is necessary to control the number of walkers and cancellation of positive and negative walkers beyond a specified age has been found effective. Applications to obtain energies of high accuracy for several systems have recently been described[53].

Some of the most interesting prospective applications are those for systems of 10 to 100 or more electrons for which the available trial wavefunctions are SCF wavefunctions.

These are easily generated along with accurate values for many of integrals required in sampling the source terms for difference calculations. The functions are relatively smooth and may allow reasonably large time-steps with minimal time-step error. An even more interesting possibility - that of an extension to correct node locations - remains an elusive but tantalizing target.

12 Excited States

Both DQMC and GFQMC provide the lowest-energy solution to the Schrödinger equation subject to any constraints which may be imposed on the solution. For excited states one must impose the necessary constraints[47]. In some cases this is relatively easy to do but in others it is difficult or as yet impossible. For these cases alternate methods are available: in particular, a matrix procedure appied to the evolution of several states at once in imaginary time[54].

The fixed-node method may be used for excited states when the nodes are known in advance as in the case of the ^{3}P helium atom for which the nodal surface occurs at $r_1 = r_2$. For electronic systems of more than two electrons such a specification cannot be made in advance, but for vibrations of diatomic and polyatomic molecules the nodes for many modes of vibration can be specified from geometric considerations. Thus, fixed-node calculations have a place in calculations for excited states – especially for the first few states of small systems.

In GFQMC calculations with exact cancellation the unique symmetry of a desired state may be imposed at each step of a calculation together with importance sampling using a trial function of the same symmetry. This procedure has been used successfully to determine energies in the region of the Jahn-Teller cusp of the H-H-H potential energy surface at which symmetric and antisymmetric potential energy surfaces cross[42,43].

One may also impose the restriction of orthogonality to a ground or other lower state if the wavefunction for that state is known. If the wavefunction for the lower state of interest is not known explicitly, it may be possible to generate it in the form of a distribution of walkers in concommitant Monte Carlo calculations and the excited state distribution may then be restricted to a (net) zero overlap with the ground state. Several example systems have been treated in this way[55].

The matrix procedure applied to the time evolution of states requires only a single distribution of walkers propagated with a guide function as in importance sampling. Using a basis set of N trial wavefunctions one obtains the evolution of N states and their energies from the matrix elements between basis functions. The variance in energies increases exponentially with number of steps as for the released-node method. Nevertheless, excellent results have been obtained for the vibrations of H_2CO with as many as eight levels of vibration each of several modes determined with very high accuracy[54].

13 Use of Pseudopotentials

Quantum Monte Carlo calculations, like analytic variational calculations, can be considerably simplified – without a great loss in accuracy – by the use of effective potentials to replace core electrons close to the nuclei. In general, it has been found as expected that

as in analytic variational calculations with effective potentials or with frozen core basis sets, the energies of the core electrons and their effect on valence electrons will be almost exactly cancelled in subtracting to obtain relative energies for nearly identical systems. Since the energies of core electrons in heavy atoms are usually very much greater than the energies of valence electrons, including core electrons in QMC calculations is very much more expensive computationally when statistical error in the total energy must be reduced. In terms of local energy the core electrons are very 'noisy' and they contribute a disproportionate share of the variance in local energies. In addition, the sharper gradients in the core region lead to a requirement of much smaller time steps for accuracy in treating core electrons. The acceptable time-step size is much larger for outer elecrons. The advantages of eliminating core electrons are large in proportion to the number of core electrons eliminated.

When core electrons are eliminated the Hamiltonian for the valence electrons of an atom becomes

$$\hat{H}_{val} = -\sum_i \frac{-Z_{eff}}{r_i} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_i \hat{W}_i \ . \tag{51}$$

where the electrons are indexed i and j, Z_{eff} is an effective nuclear charge and $\hat{W}_i$ is a pseudopotential operator for electron i.

The effective potentials normally used in analytic variational calculations are non-local potentials which involve angular projection operators which cannot be simply transferred into QMC calculations. In the earliest QMC calculations to use effective potentials Hurley and Christiansen[56] and Hammond, Reynolds, and Lester[57] avoided this difficulty with the use of local potentials defined in terms of trial wavefunctions. The use of effective potentials is, by its nature, not exact and introduces systematic errors which, in most cases thus far, have been found to be small. In later work non-local effective potentials[58–60] have been used with success as have their more-complex counterparts, effective Hamiltonians. These too introduce systematic errors of finite size, but the errors are not easily analyzed and for that reason it is difficult to make judgements about the relative merits of the several methods.

The results of calculations using effective core potentials of the several types may be compared with experimental measurements, but more useful comparisons can be made with all-electron calculations for the same systems. For example, in studying the use of effective core potentials in QMC calculations Lao and Christiansen[61] calculated the valence correlation energy for Ne and found excellent agreement with previous full-CI benchmark calculations. They recovered 98 to 100 percent of the valence correlation energy and could detect no significant error due to the effective potential approximation.

The advantage of the use of pseudopotentials is very dramatically illustrated by DQMC calculations for the Fe atom carried out by Mitas[62] for (a) all-electrons, (b) for a neon-core pseudopotential, and (c) for an argon-core pseudopotential. The relative calculation effort for a fixed statistical uncertainty was in the same order (a) 6250, (b) 60, (c) 1 . Thus, the appeal of pseudopotentials very strong. Of course, the additional (systematic) uncertainty introduced with the use of pseudopotentials is a disadvantage. Additional work will undoubtedly resolve the relative advantages and disadvantages.

A sampling of studies using effective potentials, model potentials, effective Hamiltonians, and related devices is given in Table 2. The entries range from the three-electron case

Authors	Ref.	Species
Hammond, Reynolds, and Lester (1987)	57	Li/Li^+, Na/Na^+
Hurley and Christiansen (1987)	56	Li/Li^-, K/K^-
Fahy, Wang, and Louie (1988)	63	Solid C(diamond)
Christiansen and LaJohn (1988)	64	Mg/Mg^+
Yoshida, Mizushima, and Iguchi (1988)	65	Cl/Cl^-
Carlson, Moskowitz, and Schmidt (1989)	66	Li/LiH, Li_2/2 Li
Bachelet, Ceperley, and Chiocchetti (1989)	60	Na_2/Na/Na^-/Na^+ Mg, Si, Cl dimers and ions
Fahy, Wang, and Louie (1990)	67	Solid C(diamond), solid Si
Li, Ceperley, and Martin (1991)	68	Solid Si/Si
Shirley, Ceperley, and Martin (1991)	69	Be/Be^+, Na/Na^+, Sc/SC^+
Flad, Savin, and Preuss (1992)	59	Be/Be^+, also Mg, Ca, Sr, Ba, Li, Na, K mixed dimers
Schrader, Yoshida, and Iguchi (1993)	70	PsF/Ps+F, PsCl/Ps+Cl
Belohorec, Rothstein, and Vrbik (1993)	71	CuH (several states)
Tanaka (1993)	72	Solid NiO
Rajagopal, Needs, Kenny, Foulkes, and James (1994)	73	Solid Ge
Mitas (1994)	62	Fe/Fe^+/Fe^-
Mitas and Martin (1994)	74	N, N_2, solid N, solid N_2
Grossman, Mitas, and Raghavachari (1995)	75	C_{10}, C_{20}
Greeff and Lester (1997)	76	Si_mH_n
Williamson, Rajagopal, Needs, Fraser, Foulkes, Wang, and Chou (1997)	77	Solid Si (1000 electrons)

Table 2. A sampling of QMC calculations with pseudopotentials.

of the Li atom, one of the earliest to be studied, to Cl atoms using neon-core pseudopotentials, to the atoms Al, Sc, and Fe, to clusters of Si and of silicon hydrides, to the diamond structure of solid C and Si, as well as that of GaAs.

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